



NARloy-Z-Carbon Nanotube Composites

**Seminar Presentation
Department of Mechanical Engineering
Vanderbilt University**

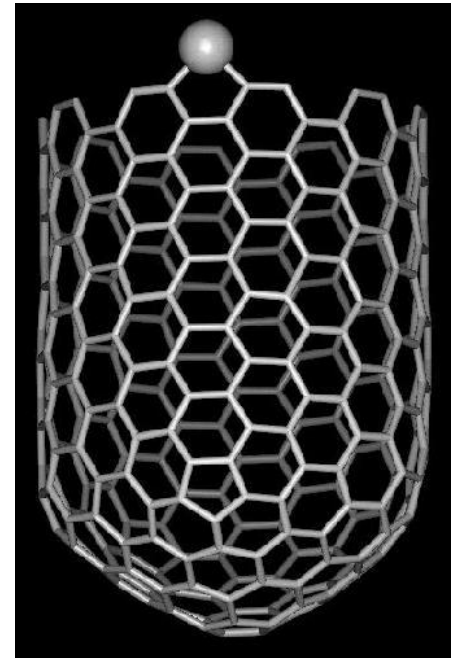
April 16, 2012

**Biliyar N. Bhat, Ph.D.
Materials and Processes Laboratory
NASA - Marshall Space Flight Center
Huntsville, AL**



NARloy-Z-Carbon Nanotube Composites

- Introduction
- Experimental approach
- Results
- Modeling
- Discussion
- Conclusions





Introduction

- Project Team:
 - Biliyar Bhat – Marshall Space Flight Center (MSFC)
 - Principal Investigator and project Manager
 - David Ellis – Glenn Research Center (GRC)
 - Co-Investigator
 - Vadim Smelyanskiy – Ames Research Center (ARC)
 - Co-Investigator
 - Jogender Singh – Applied Research Laboratory (ARL)–
Pennsylvania State University (PSU)
 - Yogesh Vohra – University of Alabama Birmingham
(UAB)
 - Members of technical staff at MSFC Materials and
Processes Laboratory



Introduction (Cont'd.)

- Motivation:
 - NARloy-Z (Cu-3%Ag-0.5%Zr) is the state of the art, high thermal conductivity structural alloy used for making liquid rocket engine main combustion chamber liner
 - Thermal conductivity ~80% of pure copper
 - Improving the thermal conductivity of NARloy-Z will help to improve the heat transfer efficiency of combustion chamber
 - Will also help to reduce the propulsion system mass and increase performance
 - Increases thrust to weight ratio
 - Improving heat transfer helps to design and build better thermal management systems for nuclear propulsion and other applications



Introduction (Cont'd.)

- Question: Can Carbon nanotubes (CNT) help to improve the thermal conductivity (TC) of NARloy-Z?
 - CNT's have TC of ~20X that of copper
 - 5vol% CNT could potentially double the TC of NARloy-Z if properly aligned
 - Improvement will be less if CNT's are randomly distributed, provided there is a good thermal bond between CNT and matrix.
- Prior research has shown poor results
 - No TC improvement in the copper-CNT composite reported
 - Reported values are typically lower
 - Attributed to high contact thermal resistance between CNT and Cu matrix
 - Results suggest that a bonding material between CNT and copper matrix is required to lower the contact thermal resistance
- It is hypothesized that Zr in NARloy-Z could act as a bonding agent to lower the contact thermal resistance between CNT and matrix



Experimental Approach

- Blending of NARloy-Z powder with multiwall CNT (MWCNT) in varying proportions
 - 1, 2, 5, 10, 20 volume percent
- Consolidation and sintering at elevated temperature to produce discs of NARloy-Z-CNT composite material, 100% density
 - Field Assisted Sintering Technology (FAST) for randomly oriented MWCNT
 - Extrusion process for aligned composite
- Evaluation of the resulting NARloy-Z-CNT composite material for mechanical and thermal properties
- Microstructure analysis and correlation with properties
- Chemistry based analysis of contact thermal resistance between CNT and NARloy-Z matrix



Blending MWCNT with NARloy-Z



Attritor Parts

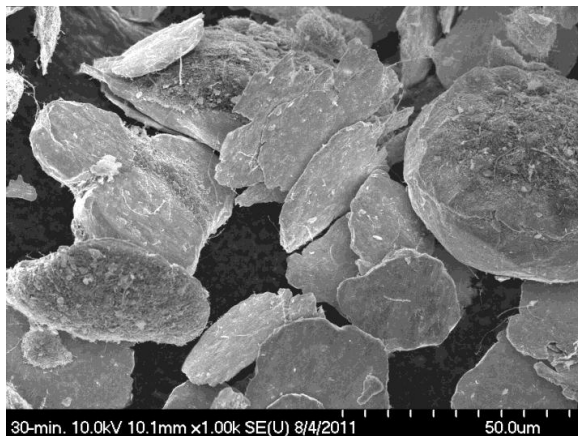


Attritor in operation

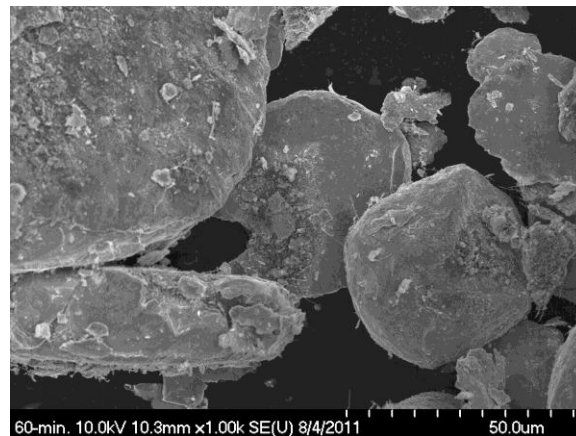
Blending was done in an attritor (shown above)
in an inert atmosphere of gaseous nitrogen



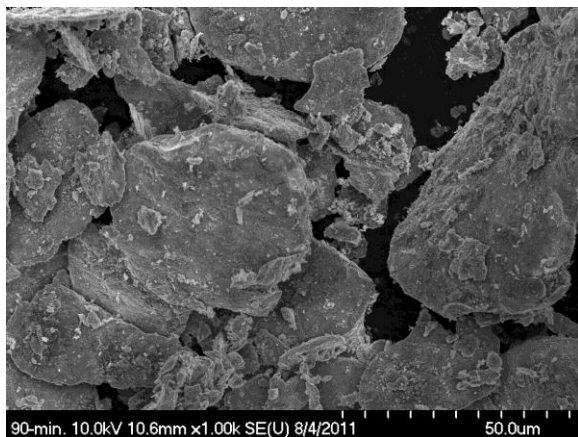
Powder Evolution During Ball Milling



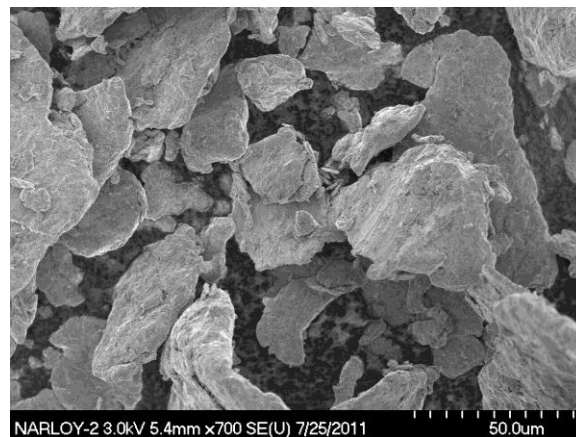
30 min



60 min



90 min

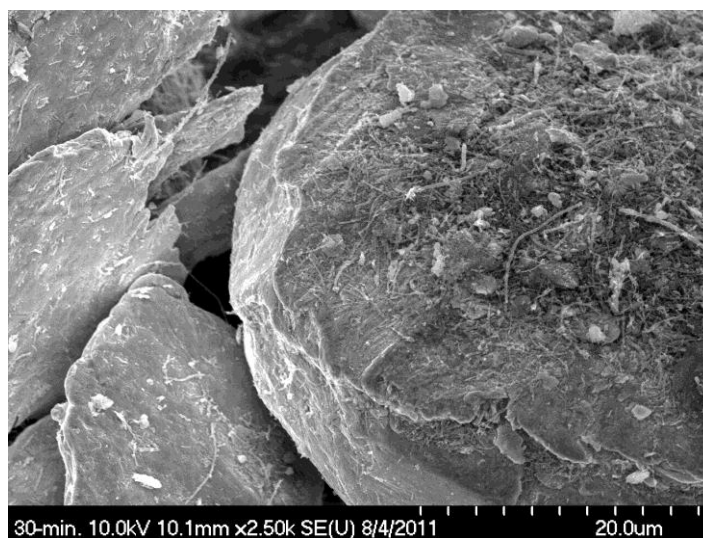
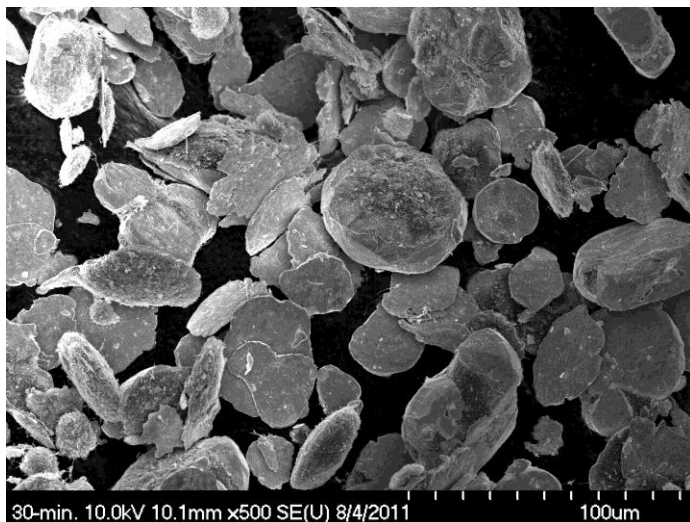


120 min

Microscopy suggests that the powders start to be ground between 90 and 120 minutes
Time limited to no more than 90 minutes to minimize damage to MWCNT



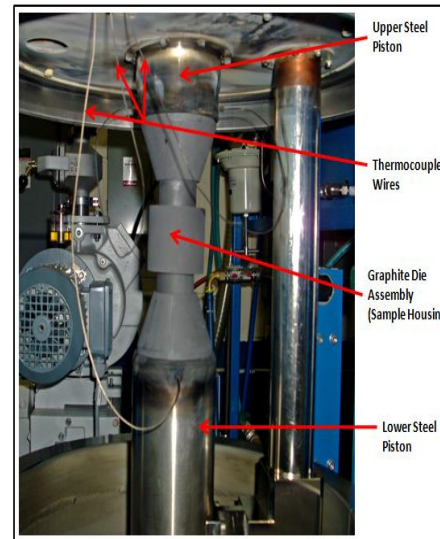
NARloy-Z-10Vol.% Multiwall CNT – 30 Minute Blending





Consolidation by FAST Process

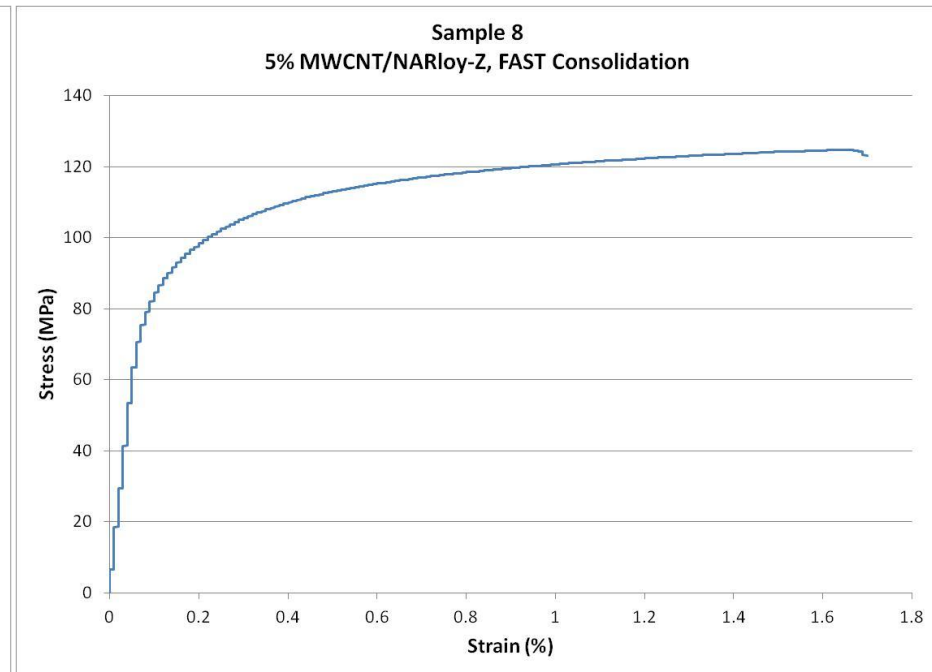
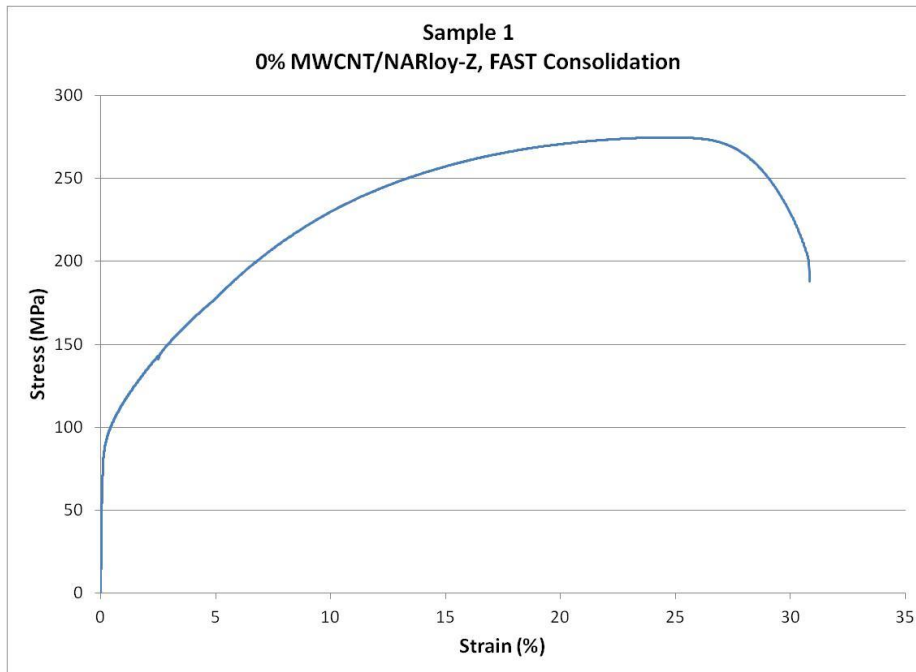
- **Field Assisted Sintering Technology (FAST) at ARL - Penn State was used for NARloy-Z-CNT blended powder consolidation in vacuum**
- **Compositions sintered:**
 - NARloy-Z (baseline), NARloy-Z-1%, 2%, 5%, 10%, 20%CNT
- **Sintering Parameters:**
 - Temperature - 975C, pressure - 65 Mpa, heating rate – 10C/min, holding time 20 minutes, furnace cooled





MWCNT/NARloy-Z Tensile Properties

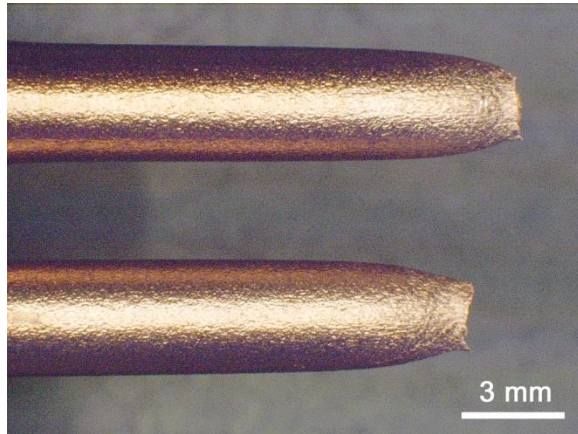
% MWCNT	Average Yield (MPa)	Average UTS (MPa)	Average Elongation (%)	Average R.A. (%)
0	88.2	271.7	31.3	61.2
5	105.9	124.7	1.6	1.2
10	97.8	107.5	0.8	0.8



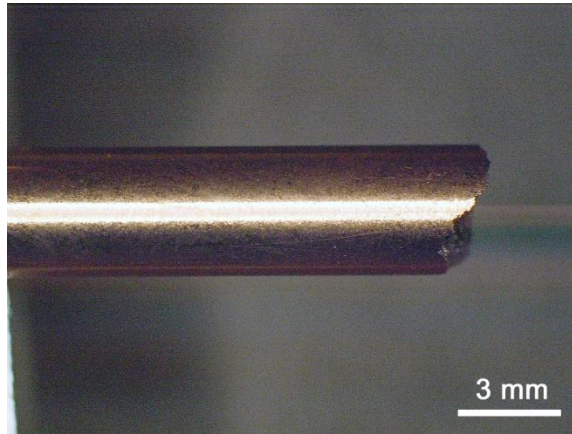
Note: FAST NARloy-Z samples have lower UTS, comparable YS to wrought NARloy-Z. MWCNT containing samples fail shortly after yielding but have good yield strengths.



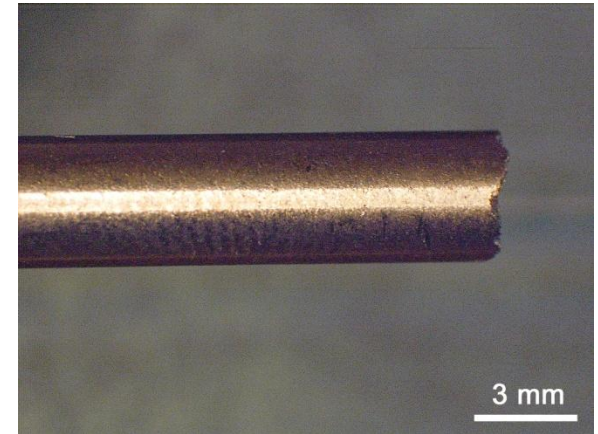
MWCNT/NARloy-Z Tensile Test Specimens



0% MWCNT
(NARloy-Z)



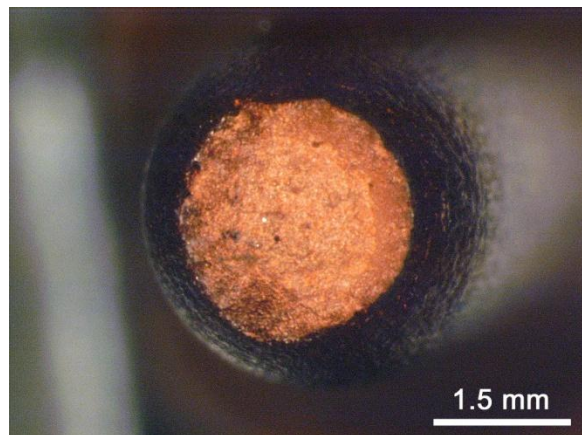
5% MWCNT



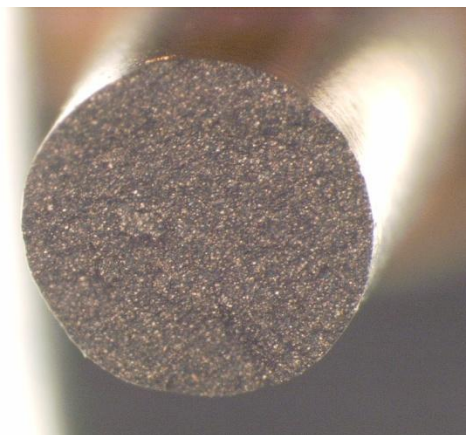
10% MWCNT



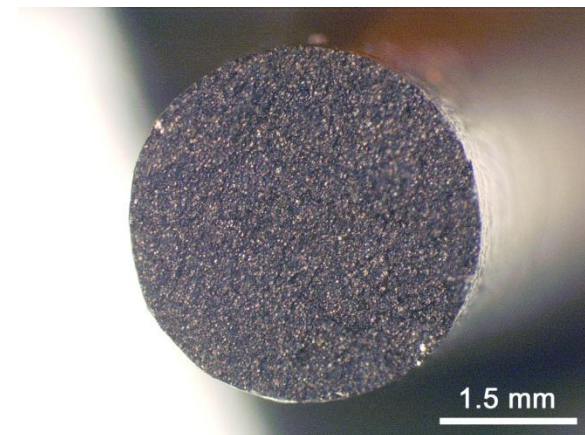
MWCNT/NARloy-Z Tensile Fracture Surfaces



0% MWCNT
(NARloy-Z)



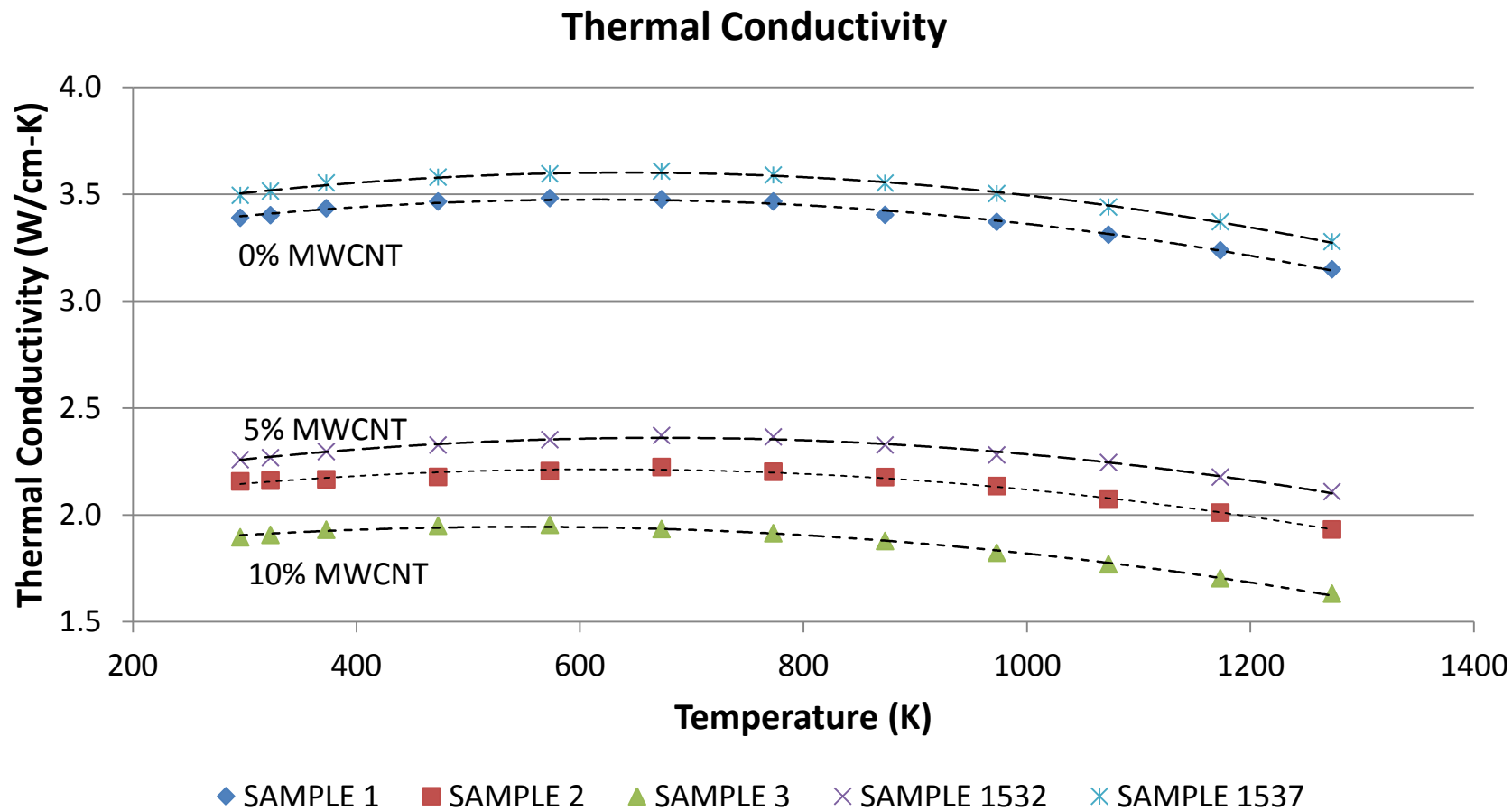
5% MWCNT



10% MWCNT

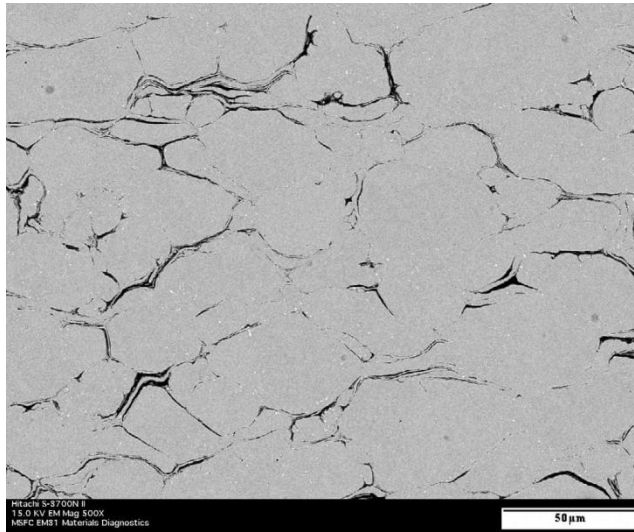


Thermal Conductivity Results (TPRL)

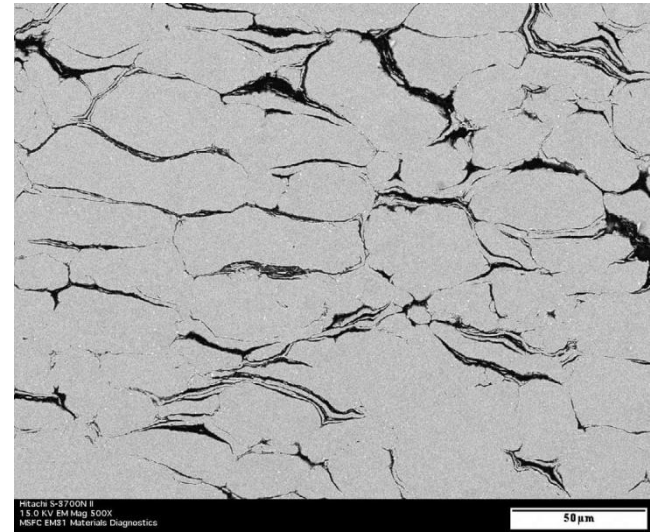




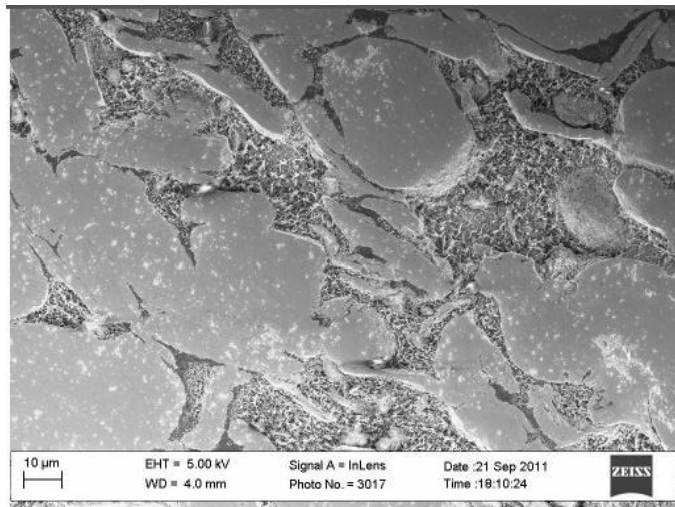
Microstructure - FESEM



NARloy-Z-5%CNT



NARloy-Z-10%CNT



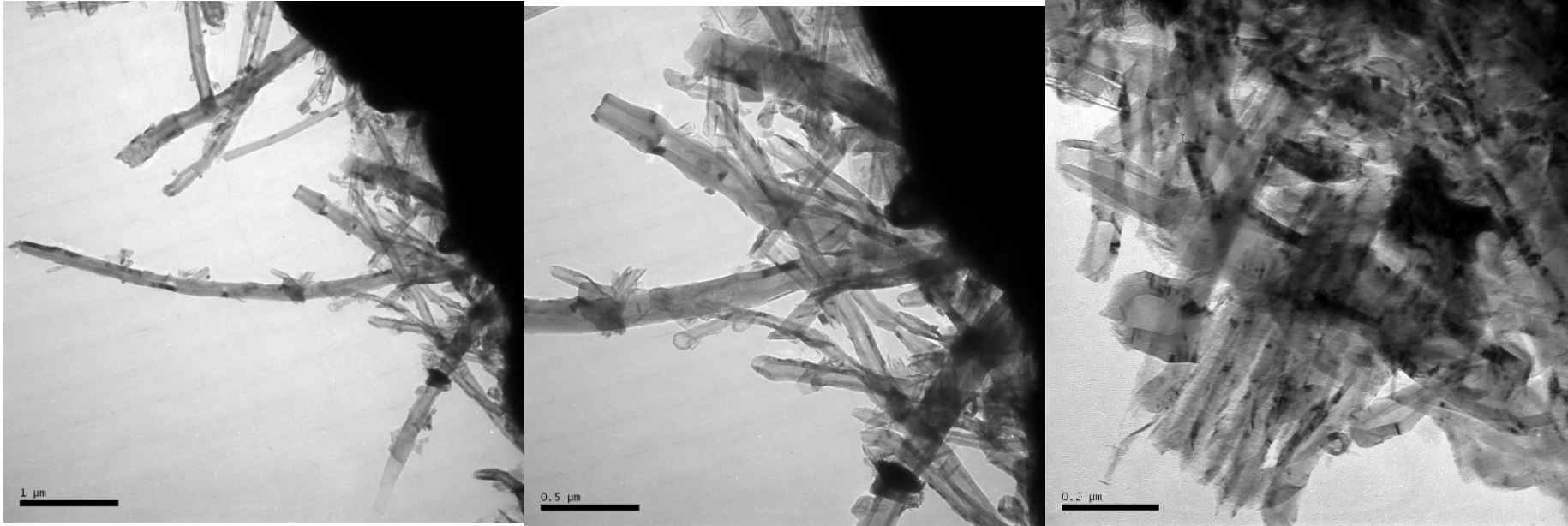
1544 NARloy + 20%vol CNT FESEM

NARloy-Z-20%CNT

Note the inter-granular segregation of CNT in grain boundaries in all cases



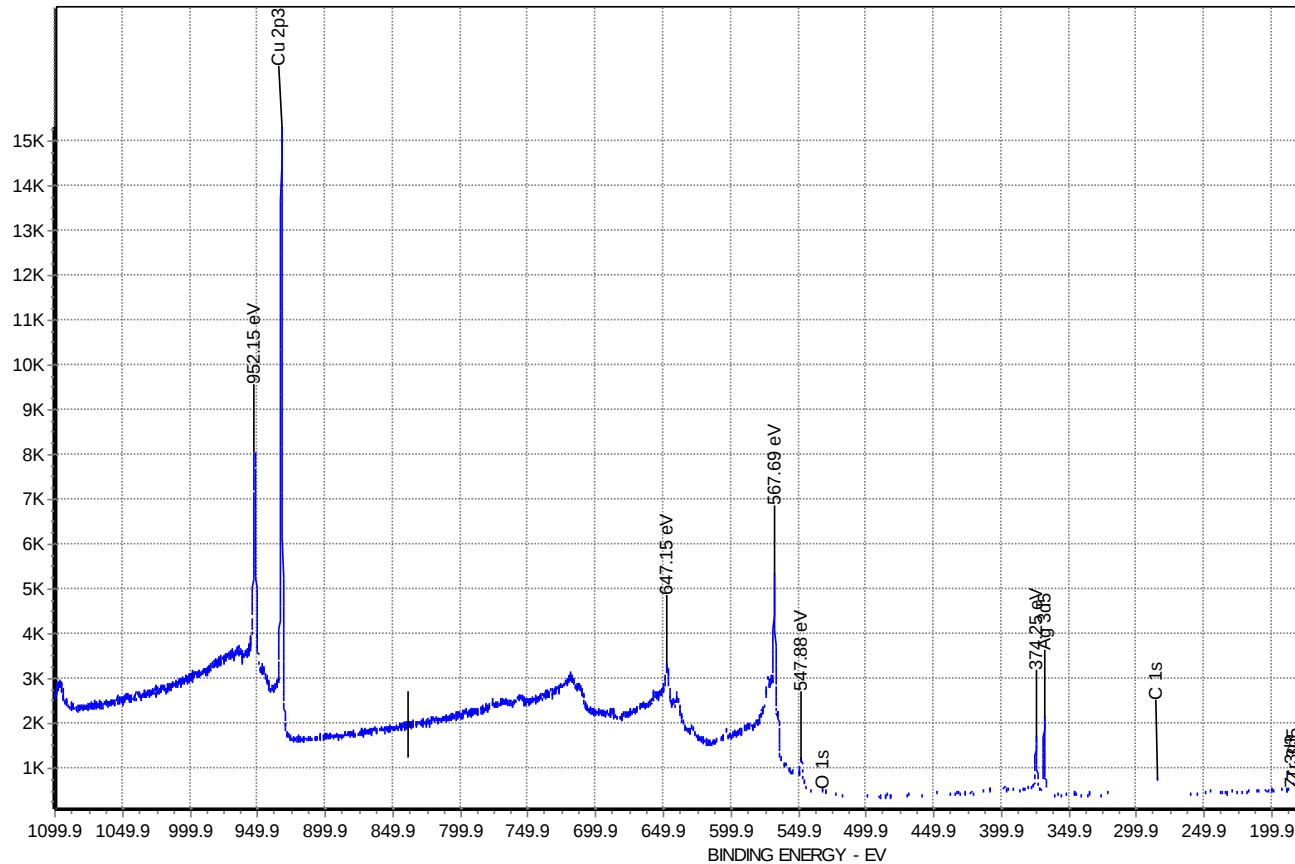
Microstructure - TEM



NARloy-Z-5%CNT Composite: matrix-CNT interface area



ESCA Analysis: NARloy-Z-10%CNT



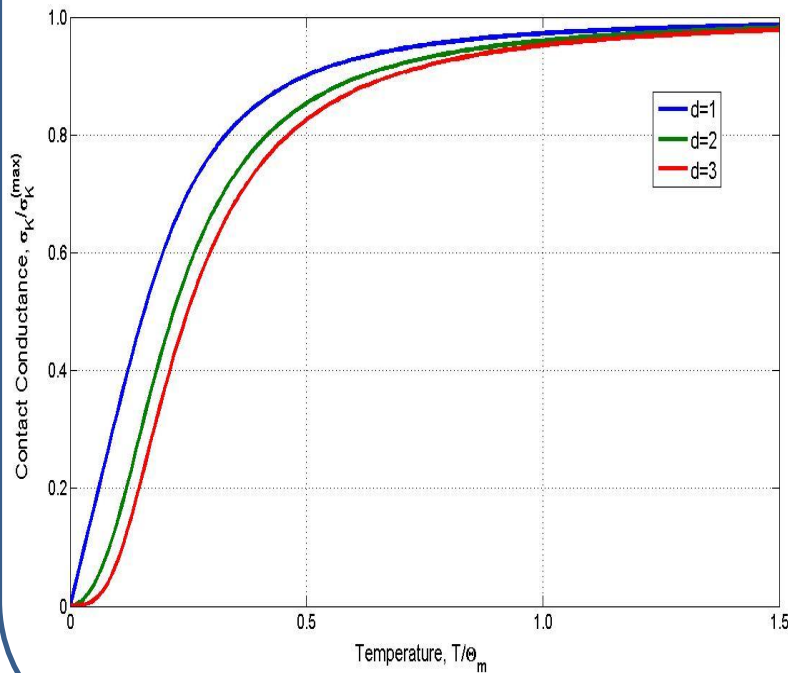
Note: Analysis shows lack of ZrC



Chemistry Based Modeling of NARloy-Z-CNT Composite: Analysis of Contact Thermal Resistance

(M. Foygel and V. N. Smelyanskiy , NASA ARC)

Contact Conductance of Metals with Carbon Modifications: $d = 1$ (CNT), $d=2$ (graphene, G), $d = 3$ (diamond, D)



Parameter Contact	θ_m, K	$\sigma^{max}, kW/cm^2K$
D/Cu	310	6.6
D/Zr	250	3.5
D/Ag	221	2.4
D/ZrC	680	70
ZrC/Cu	310	35
D/ZrC/Cu	680, 310	23
CNT/Cu	310	$8.9 \cdot 10^{-13}, kW/K$
G/Cu	310	$2.6 \cdot 10^{-6}, kW/cm \cdot K$



Chemistry Based Modeling of NARloy-Z-CNT Composite: Analysis of Contact Thermal Resistance_(Cont'd.)

(M. Foygel and V. N. Smelyanskiy , NASA ARC)

- The composite CNT/ZrC/Cu has contact thermal resistance **3.5 times smaller** than that of the direct CNT/Cu contact.
 - Composite CNT/Zr/Cu or CNT/Ag/Cu contacts will have higher thermal resistance compared with the direct CNT/Cu one.
- In NarloyZ-CNT composites, the input to the thermal conductivity from the CNTs, whose length exceeds 10 microns is not likely to be dominated by contact resistance. (In other words, longer CNTs should be preferred.)
- That critical CNT length may be reduced further (by 3X) if the CNT surfaces are covered with a (mono)layer of material, such as ZrC or Cr_3C_2 with Debye's temperature greater than that of copper.



Discussion

- Microstructures clearly show that the MWCNT did not blend well with NARloy-Z powder
 - MWCNT clumps were not broken up
 - Longer grinding times tended to grind the CNT, did not break up the clumps
- Microstructure is broken up by the MWCNT clumps resulting in lower thermal conductivity
 - Similar results reported by other investigators in other metal systems – Cu, Al
- There appears to be lack of bond between CNT and matrix
 - No ZrC is detected in the ESCA analysis

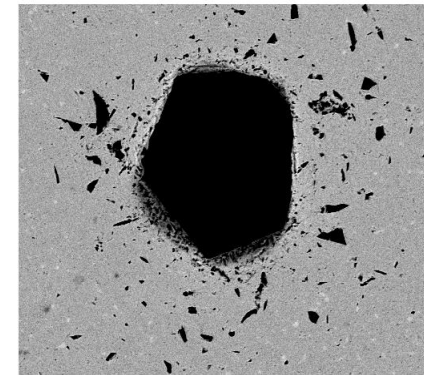
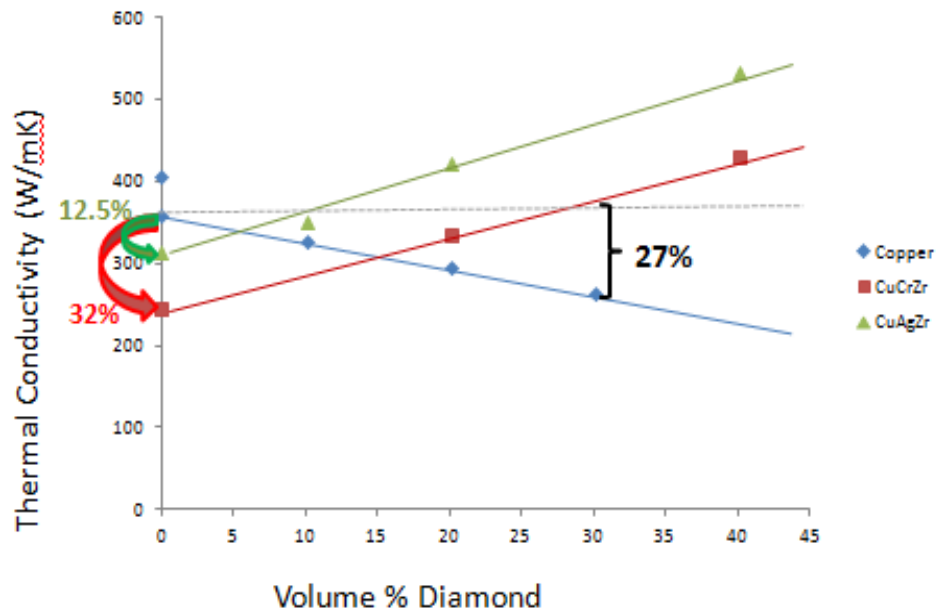


Approach to Problem Resolution

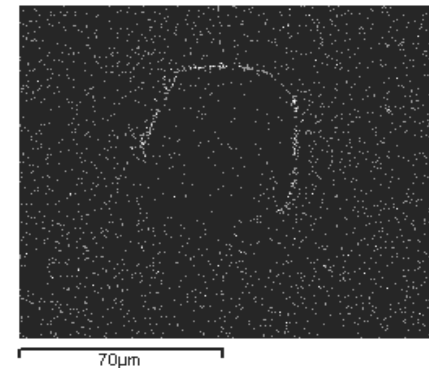
- Separate the MWCNTs and keep them separated such that they do not agglomerate
- Make sure there is sufficient Zr where it is needed for bonding
 - at the CNT-NARloy-Z matrix interface
 - Can be accomplished by coating the CNTs by Zr
- Modeling work also suggests that an interlayer of Zr or Cr should help to reduce contact thermal resistance
- Experimental evidence in Cu-Zr-Diamond system suggests that this approach might work – next chart
- May need an overcoat of copper to prevent oxidation of coating (especially Zr) during handling and transport



Evidence of Zr Interlayer in CuAgZr-Diamond System (ARL- PSU)



CuAgZr-D Composite

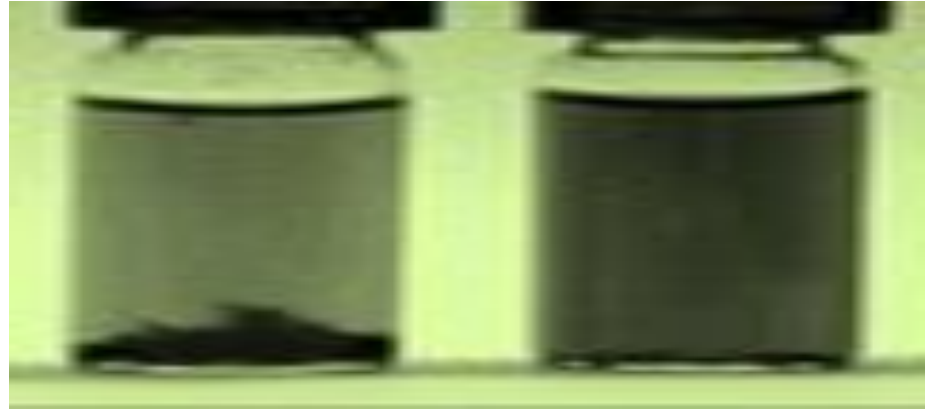


EDS mapping of Zr

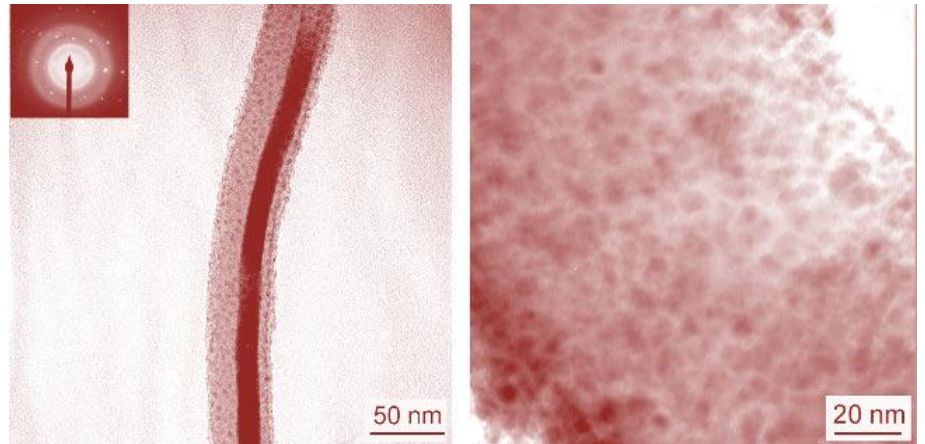


CNT Separation (UAB)

Step 1: Obtain dispersibility of CNTs by Carboxylic acid group functionalization



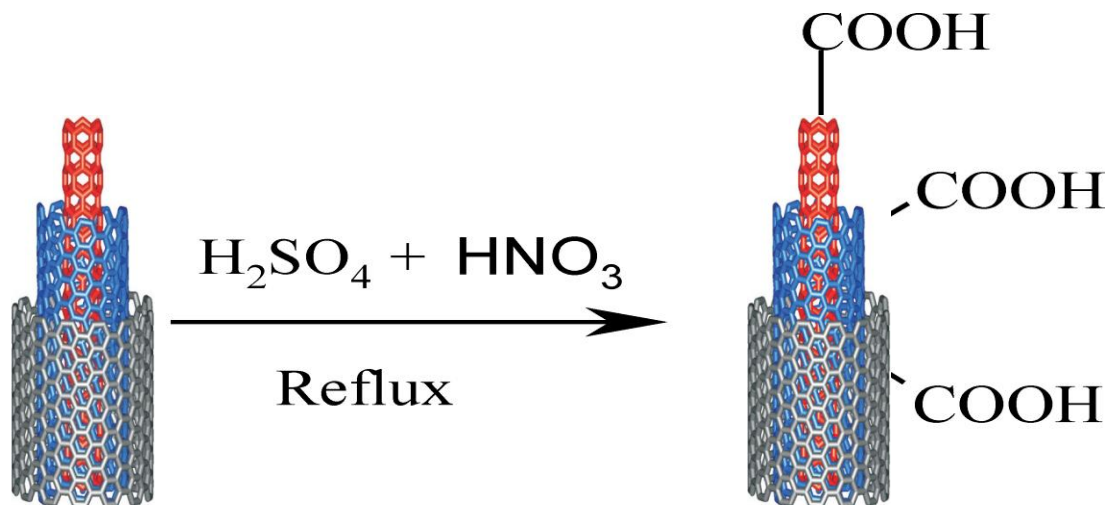
Step 2. Chromium or Zirconium metallization of CNTs by wet chemical methods or by vapor phase methods.





Separation of CNTs by Acid modification

- Carboxylated CNTs disperse well in media

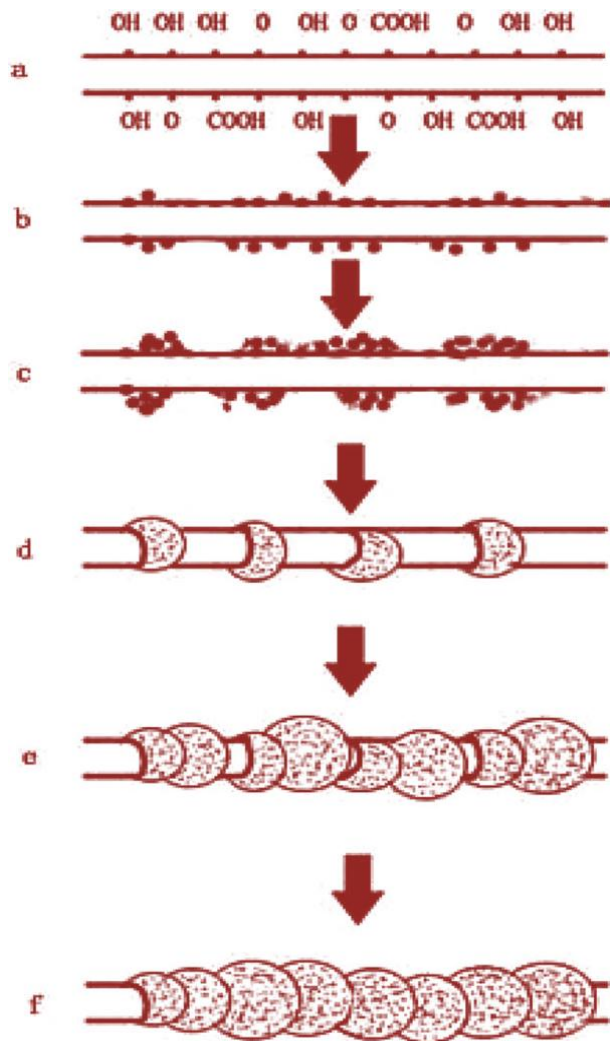


Surface-oxidization of CNTs by 70 % HNO_3 at 110°C - 130°C for 6-12 h

If necessary, other functional groups such as $-\text{NH}_2$ can be attached using standard chemical reactions.



Electroless Plating of Zr



Oxidized CNTs

Activation by (0.1 M SnCl_2 + 0.1 M HCl) sonication for 1h

Activation by (0.0014M PdCl_2 -0.25M HCl for 30 min)

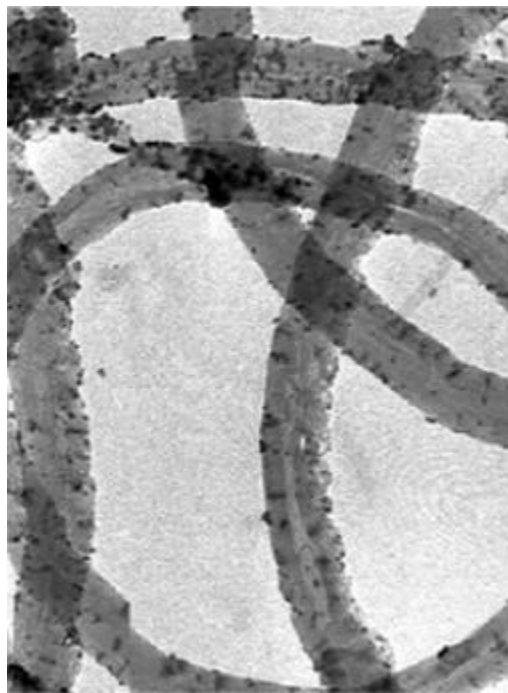
Electroless deposition of metal using metal salt solution

Reduction the metal ions by NaBH_4 , HCHO or ethylene glycol at 80°C .

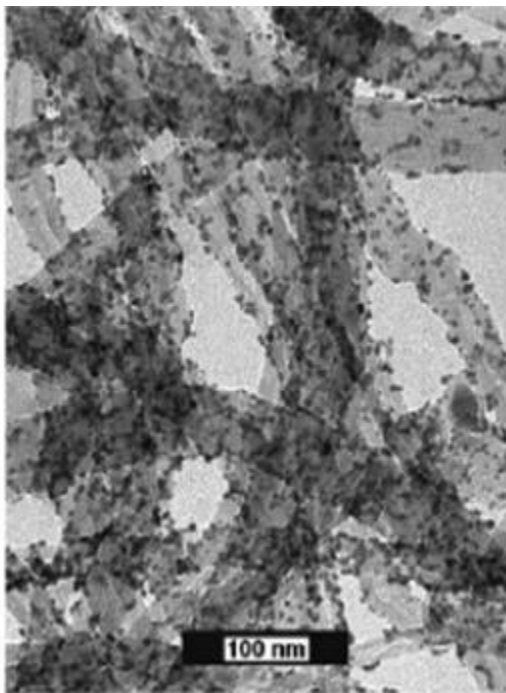
By changing the metal salt solution concentration a uniform coating can be achieved



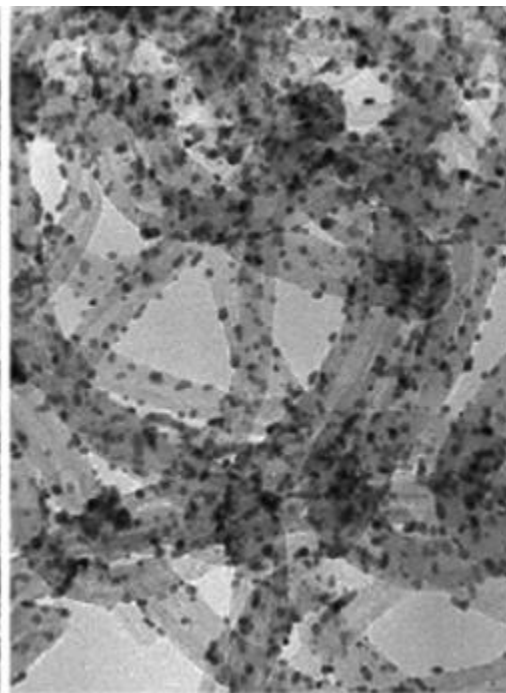
Platinum Coated CNT by Electroless Plating



10%



20%



30%



Conclusions

- The technique of blending MWCNT with NARloy-Z powder and consolidating it at elevated temperatures did not result in improved thermal conductivity of NARloy-Z
- Two probable causes were identified:
 - Agglomeration of MWCNT at prior particle boundaries, which breaks up the microstructure
 - Lack of good contact thermal resistance between CNT and NARloy-Z matrix
- Yield strengths of NARloy-Z-CNT composites were comparable to the baseline NARloy-Z, but the ultimate strength and ductility were significantly lower
 - Results correlate well with microstructure
- Follow on work addresses these issues
 - Separation of CNTs to prevent agglomeration
 - Coating the CNTs (with Zr) to ensure thermal bonding
- Chemistry based modeling supports the planned approach
 - Supports the need for a layer of bonding material at the CNT-NARloy-Z interface